

analogous to our earlier definition. Indeed, in our earlier definition all quantum states were non-degenerate, so the summation can equally well be ~~over~~ over all the quantum states ~~S~~

$$(\text{originally}) \quad Z = \sum_{S} e^{-E_S/kT} = \sum_S e^{-E_S/kT}$$

We can see that the same formula will give our new partition function, since now to each energy  $E_S$  there correspond  $d(E_S)$  states with the same energy and so

$$\sum_S e^{-E_S/kT} = \sum_{E_S} d(E_S) e^{-E_S/kT} = Z \quad (\text{new})$$

$$(1) \quad \text{Hence, in any case } Z = \sum_S e^{-E_S/kT}$$

Also, before the probability <sup>(\*)</sup> to be in a given quantum state  $S$  and to be at a certain energy  $E_S$  were equal since there was only one state per energy. But now there are  $d(E_S)$  states ~~per~~ for each  $E_S$ , so

$$p_S = \frac{1}{d(E_S)} p(E_S)$$

Applying (\*) and using  $\text{const} = \frac{1}{Z}$ , we get:

$$p_S = \frac{1}{d(E_S)} \frac{1}{Z} d(E_S) e^{-E_S/kT} = \frac{1}{Z} e^{-E_S/kT}$$

$$(2) \quad p_S = \frac{1}{Z} e^{-E_S/kT} \quad - \text{again the same formula as before}$$

So formulas (1) and (2) are correct even for degenerate energies — just remember that  $S$  represents a given state, not a given energy!

(2.) Kittel 3.1

$$(a) Z = \sum_S e^{-E_S/kT} = e^{-0/kT} + e^{-E/kT} = 1 + e^{-E/kT}$$

$$F = -\tau \ln Z = \boxed{-\tau \ln (1 + e^{-E/kT})}$$